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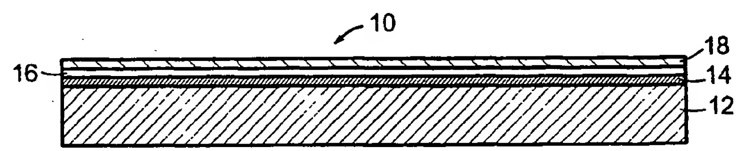
(54) Title: COATED CONDUCTOR THICK FILM PRECURSOR



(57) Abstract: Methods for preparing thick film rare-earth $Ba_2Cu_3O_{7-\delta}$ (such as YBCO) superconductive layers, particularly including deposition of a precursor as a dispersion of solid-state materials, including a binder or a solvent or both constituents. The solid-state materials include oxides, fluorides, and acetates of yttrium, barium, and copper in the form of ultrafine particles.

WO 01/08236 A1

Coated Conductor Thick Film Precursor

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TECHNICAL FIELD

This invention relates to high temperature superconductors (HTS), and more particularly to superconducting layers and methods of depositing precursor compositions for such layers.

BACKGROUND

Coated conductors, comprising a single or multiple combinations of a biaxially textured high temperature superconductor ("HTS") layer on a thin buffer layer and a substrate tape, are a cost-performance-effective technology for manufacturing long length flexible HTS wire for magnet, coil and power applications. For example, these conductors should be useful for power transmission cables, rotor coils of motors and generators, and windings of transformers, as well as for magnets for medical magnetic resonance imaging (MRI), magnetic separation, ion-beam steering and magnetic levitation. Particularly of interest here are applications which use ac currents and fields, or fast ramps of current and field, for example ac power transmission cables, transformers, faultcurrent limiters, magnetic separation magnets and high energy physics magnets.

Some background on biaxially textured high temperature superconducting "coated conductors" is known. Such coated conductors include at least, for example, a substrate and a superconducting layer (such as YBCO) deposited thereon. One or more buffer layers may be included between the substrate and the superconductor material. An advantage of such materials as YBCO ($YBa_2Cu_3O_x$, or Yttrium-Barium-Copper-Oxide) films is the very high critical current densities attainable, particularly in magnetic fields. Other related superconducting materials which can be used are $REBa_2Cu_3O_x$, where the Y has been partially or completely replaced by rare earth elements (RE). As information as to the requirements for commercial application, and limitations on conductor technology has become available, the potential for low

production costs of these rare-earth superconducting materials (including YBCO) has also become of interest in further development.

Certain challenges in this field include the need for cost effective methods for producing chemically compatible biaxially textured buffer layers, as well as the need to deposit sufficient thickness of the high critical current density superconducting layer. Regarding the first objective, it appears that deformation textured substrates with epitaxial buffer layers can be made cost effective. In addition ion beam assisted deposition of thin MgO layers with epitaxial top layers may prove to be economically viable.

Regarding the need to deposit thick layers of superconductor precursor compositions, a number of techniques have been evaluated. Chemical vapor deposition (CVD) is not considered a competitive method at this time, due to the very high cost of precursor materials. Most physical vapor deposition (PVD) methods, (for example, pulsed laser ablation, reactive sputtering and electron beam evaporation) are limited by deposition rate, compositional control, and high capital costs. A possible economical PVD method would be thermal or electron beam evaporation of the rare earth elements, copper and barium fluoride, known as the "barium fluoride" process. This process appears to be more rapid than direct PVD methods, but capital costs and control system costs are still likely to be too high. Additionally, the deposited precursor composition must subsequently be reacted in a separate furnace system to form the HTS film.

Solution deposition methods have been evaluated, and these appear to offer much lower costs, since vacuum systems are eliminated. Thus, capital costs are not as high, and deposition rates not as low, as other methods using vacuum systems. Trifluoroacetate (TFA) solution processes offer low costs for precursor compositions, high deposition rate, and non-vacuum processing advantages. Such processes are described, for example, in U.S. Patent No. 5,231,074 to Cima et al., and PCT Publication No. WO 98/58415, published December 23, 1998 and require dissolution of the constituents of the precursor composition to form a solution phase.

For commercial processes, it is desirable to have a composition serving as a precursor to superconducting films, which can be coated onto large area substrates in

a single application using high-deposition rate, to produce a desired film thickness. The precursor composition is preferably convertible to the superconducting phase by way of simple thermal processes.

SUMMARY

The invention provides a low cost method for fabricating thick film precursor compositions of rare-earth superconductors on long lengths of substrate. The final thicknesses of such films are preferably between about 1 micron and about 5 microns. The specific superconductors of interest are high temperature superconductors of the class of rare-earth barium cuprate species (REBCO), including, for example, $YBa_2Cu_3O_{7-x}$ (YBCO), or systems based on thallium/barium/calcium/copper/oxide (ThBCCO) or bismuth/strontium/calcium/copper/oxide (BSCCO), and other known superconducting materials, including versions doped with other species. Of particular interest are those materials having superconducting transition temperatures, $T_{c,}$ above about 77 K. The most useful buffered substrates for such films are biaxially textured, providing an epitaxial growth template for achieving maximum attainable critical current densities (J_c). The precursor compositions for the superconducting layer of such high temperature superconductors include solid-state, or semi solid-state precursors deposited in the form of a dispersion . These precursor compositions allow for example the substantial elimination of in the case of YBCO $BaCO_3$ formation in final YBCO superconducting layers, while also allowing control of film nucleation and growth.

As used herein, "biaxially textured" refers to a surface for which the crystal grains are in close alignment with a direction in the plane of the surface. One type of biaxially textured surface is a cube textured surface, in which the crystal grains are also in close alignment with a direction perpendicular to the surface. Examples of cube textured surfaces include the (100)[001] and (100)[011] surfaces, and an example of a biaxially textured surface is the (113)[211] surface. As used herein, "epitaxial layer" refers to a layer of material, the crystallographic orientation of which is directly related to the crystallographic orientation of the surface of a layer of material onto which the epitaxial layer is deposited. For example, for a multi-layer superconductor having an epitaxial layer of superconductor material deposited onto a

substrate, the crystallographic orientation of the layer of superconductor material is directly related to the crystallographic orientation of the substrate. Thus, in addition to the above-discussed properties of a substrate, it can also be desirable for a substrate to have a biaxially textured surface or a cube textured surface.

As used herein, a "dispersion" is a two-phase system in which one phase includes finely divided particles distributed throughout a liquid second phase. As used herein, "ultrafine particles" are those particles sufficiently small to allow a uniform distribution of cation elements within the precursor composition, and a chemically homogeneous superconducting film. For a superconducting film of from about 1 to about 10 microns thickness, the particle diameters are typically less than about 10% of the final film thickness. In addition, the particle sizes are small enough, and uniformly distributed enough, to allow rapid local diffusion of cationic constituents of the precursor compositions, for the efficient formation of substantially stoichiometric superconducting layers. As used herein, "substantially stoichiometric" refers to the elemental ratios in mixtures of materials, in which the atomic ratios of cationic elements are within about 10% of whole number values. Such deviations from whole number stoichiometries can be deliberately introduced or can arise from the supply of materials, and can be desirable to aid in material processing. Experiments can show that excess elements are typically rejected by the material as a whole, resulting in nearly stoichiometric amounts of the elements.

The invention allows the deposition of thick films in a single deposition step. Although multiple deposition steps can be carried out according to the particular application, each of said steps can give a film thicker than that available from previously known solution processes. Simplified binder removal or decomposition may significantly improve the prospect of a low cost superconductor preparation method.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described below. In case of conflict, the

present specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

Other features and advantages of the invention will be apparent from the following detailed description, and from the claims.

BRIEF DESCRIPTION OF DRAWINGS

Figs. 1-3 are alternate configurations for high temperature superconductor coated conductors.

Figs. 4-6 are furnace profile diagrams used for decomposition of samples according to particular embodiments of the invention.

Fig. 7 is a furnace profile diagram used for decomposition of a prior art sample.

Fig. 8 is a Θ-2Θ X-ray diffraction spectrum of a sample according to a particular embodiment of the invention.

Fig. 9 is a Θ-2Θ X-ray diffraction spectrum of a prior art sample.

Fig. 10 is a furnace profile diagram used for reaction of samples according to particular embodiments of the invention.

Fig. 11 is a Θ-2Θ X-ray diffraction spectrum of a sample according to a particular embodiment of the invention.

Fig. 12 is a Θ-2Θ X-ray diffraction spectrum of a prior art sample.

Fig. 13 is an expanded scale view of Fig. 11.

Fig. 14 is an expanded scale view of Fig. 12.

Figs. 15-16 are pole figures for samples according to particular embodiments of the invention.

Fig. 17 is a pole figure for a prior art sample.

Fig. 18 is a plot of elemental molar ratios taken at different locations on a sample tape according to a particular embodiment of the invention.

Fig. 19 is a Θ-2Θ X-ray diffraction spectrum of decomposed samples according to particular embodiments of the invention.

Fig. 20 is a Θ-2Θ X-ray diffraction spectrum of reacted samples according to particular embodiments of the invention.

DETAILED DESCRIPTION

The invention results from the discovery that relatively high critical current densities can be achieved in high temperature superconductors (HTS) from precursor compositions containing solid-state constituents. Such methods combine the advantages of the use of a BaF_2–containing precursor composition with an easily practiced deposition method for creating thick films.

The invention includes precursor compositions, and methods for depositing precursor compositions of superconducting material on substrates, either directly onto the substrate, or onto a buffer- and/or intermediate-coated substrate, thereby forming biaxially textured superconducting oxide films from the precursor compositions. The precursor compositions comprise solid-state constituent-containing components.

Referring to Figs. 1-3, various embodiments for HTS coated conductors are shown. Referring to Fig. 1, high temperature superconductor (HTS) articles such as 10, particularly in the form of wires or tapes, generally comprise a substrate 12, at least one buffer coating 14, a superconducting layer 16 (formed of, for example, YBC, REBC), and a cap layer 18. Layer 14 can be formed of any material capable of supporting layer 16. For example, layer 14 can be formed of a buffer layer material. Examples of buffer layer materials include metals and metal oxides, such as silver, nickel, TbO_x, GaO_x, CeO_2, yttria-stabilized zirconia (YSZ), Y_2O_3, $LaAlO_3$, $SrTiO_3$, $LaNiO_3$, Gd_2O_3, $LaCuO_3$, $SrRuO_3$, $NdGaO_3$, $NdAlO_3$ and nitrides as known in the art. A buffer material can be prepared using solution phase techniques, including metalorganic deposition, such as disclosed in, for example, S.S. Shoup et al., J. Am. Cer. Soc., vol. 81, 3019; D. Beach et al., Mat. Res. Soc. Symp. Proc., vol. 495, 263 (1988); M. Paranthaman et al., Superconductor Sci. Tech., vol. 12, 319 (1999); D.J. Lee et al., Japanese J. Appl. Phys., vol. 38, L178 (1999) and M.W. Rupich et al., I.E.E.E. Trans. on Appl. Supercon. vol. 9, 1527.

Any of the embodiments can further include a cap layer 18. Cap layer 18 can be formed of one or more layers, and preferably includes at least one noble metal layer. "Noble metal," as used herein, is a metal, the reaction products of which are thermodynamically unstable under the reaction conditions employed to prepare the HTS tape. Exemplary noble metals include, for example, silver, gold, palladium, and

platinum. Noble metals provide a low interfacial resistance between the HTS layer and the cap layer. In addition, cap layer 18 can include a second layer of normal metal (for example, copper or aluminum or alloys of normal metals.

The substrate can be formed of alloys having one or more surfaces that are biaxially textured (e.g., (113)[211]) or cube textured (e.g., (100)[001] or (100)[011]). The alloys can have a relatively low Curie temperature (e.g., at most about 80K, at most about 40K, or at most about 20K).

In certain embodiments, the substrate is a binary alloy that contains two of the following metals: copper, nickel, chromium, vanadium, aluminum, silver, iron, palladium, molybdenum, gold and zinc. For example, a binary alloy can be formed of nickel and chromium (e.g., nickel and at most 20 atomic percent chromium, nickel and from about five to about 18 atomic percent chromium, or nickel and from about 10 to about 15 atomic percent chromium). As another example, a binary alloy can be formed of nickel and copper (e.g., copper and from about five to about 45 atomic percent nickel, copper and from about 10 to about 40 atomic percent nickel, or copper and from about 25 to about 35 atomic percent nickel). A binary alloy can further include relatively small amounts of impurities (e.g., less than about 0.1 atomic percent of impurities, less than about 0.01 atomic percent of impurities, or less than about 0.005 atomic percent of impurities).

In some embodiments, the substrate contains more than two metals (e.g., a ternary alloy or a quarternary alloy). In these embodiments the alloy can contain one or more oxide formers (e.g., Mg, Al, Ti, Cr, Ga, Ge, Zr, Hf, Y, Si, Pr, Eu, Gd, Tb, Dy, Ho, Lu, Th, Er, Tm, Be, Ce, Nd, Sm, Yb and/or La, with Al being the preferred oxide former), as well as two of the following metals: copper, nickel, chromium, vanadium, aluminum, silver, iron, palladium, molybdenum, gold and zinc. The alloys can contain at least about 0.5 atomic percent oxide former (e.g., at least about one atomic percent oxide former, or at least about two atomic percent oxide former) and at most about 25 atomic percent oxide former (e.g., at most about 10 atomic percent oxide former, or at most about four atomic percent oxide former). For example, the alloy can include an oxide former (e.g., at least about 0.5 aluminum), from about 25 atomic percent to about 55 atomic percent nickel (e.g., from about 35 atomic percent to about

55 atomic percent nickel, or from about 40 atomic percent to about 55 atomic percent nickel) with the balance being copper. As another example, the alloy can include an oxide former (e.g., at least about 0.5 atomic aluminum), from about five atomic percent to about 20 atomic percent chromium (e.g., from about 10 atomic percent to about 18 atomic percent chromium, or from about 10 atomic percent to about 15 atomic percent chromium) with the balance being nickel. The alloys can include relatively small amounts of impurities (e.g., less than about 0.1 atomic percent of impurities, less than about 0.01 atomic percent of impurities, or less than about 0.005 atomic percent of impurities).

An alloy can be produced by, for example, combining the constituents in powder form, melting and cooling or, for example, by diffusing the powder constituents together in solid state. The alloy can then be formed by deformation texturing (e.g, annealing and rolling, swaging, extrusion and/or drawing) to form a textured surface (e.g., biaxially textured or cube textured). Alternatively, the alloy constituents can be stacked in a jelly roll configuration, and then deformation textured. In some embodiments, a material with a relatively low coefficient of thermal expansion (e.g, Nb, Mo, Ta, V, Cr, Zr, Pd, Sb, NbTi, an intermetallic such as NiAl or Ni_3Al, or mixtures thereof) can be formed into a rod and embedded into the alloy prior to deformation texturing.

These methods are described in commonly owned U.S. Patent Application No. 09/283,775, filed March 31, 1999, and entitled "Alloy Materials;" commonly owned U.S. Patent Application No. 09/283,777, filed March 31, 1999, and entitled "Alloy Materials;" PCT Publication No. WO 99/17307, published on April 8, 1999, and entitled "Substrates with Improved Oxidation Resistance;" and PCT Publication No. WO 99/16941, published on April 8, 1999, and entitled "Substrates for Superconductors".

In some embodiments, stable oxide formation can be mitigated until a first epitaxial (for example, buffer) layer is formed on the biaxially textured alloy surface, using an intermediate layer disposed on the surface of the substrate. Intermediate layers suitable for use in the present invention include those epitaxial metal or alloy layers that do not form surface oxides when exposed to conditions as established by

P_{O2} and temperature required for the initial growth of epitaxial buffer layer films. In addition, the buffer layer acts as a barrier to prevent substrate element(s) from migrating to the surface of the intermediate layer and forming oxides during the initial growth of the epitaxial layer. Absent such an intermediate layer, one or more elements in the substrate would be expected to form thermodynamically stable oxide(s) at the substrate surface which could significantly impede the deposition of epitaxial layers due to, for example, lack of texture in this oxide layer.

In some embodiments, the intermediate layer is transient in nature. "Transient," as used herein, refers to an intermediate layer that is wholly or partly incorporated into or with the biaxially textured substrate following the initial nucleation and growth of the epitaxial film. Even under these circumstances, the intermediate layer and biaxially textured substrate remain distinct until the epitaxial nature of the deposited film has been established. The use of transient intermediate layers may be preferred when the intermediate layer possesses some undesirable property, for example, the intermediate layer is magnetic, such as nickel.

Exemplary intermediate metal layers include nickel, gold, silver, palladium, and alloys thereof. Impurities or alloys may include alloys of nickel and/or copper. Epitaxial films or layers deposited on an intermediate layer can include metal oxides, chalcogenides, halides, and nitrides. In preferred embodiments, the intermediate metal layer does not oxidize under epitaxial film deposition conditions.

Care should be taken that the deposited intermediate layer is not completely incorporated into or does not completely diffuse into the substrate before nucleation and growth of the initial buffer layer structure causes the epitaxial layer to be established. This means that after selecting the metal (or alloy) for proper attributes such as diffusion constant in the substrate alloy, thermodynamic stability against oxidation under practical epitaxial buffer layer growth conditions and lattice matching with the epitaxial layer, the thickness of the deposited metal layer has to be adapted to the epitaxial layer deposition conditions, in particular to temperature.

Deposition of the intermediate metal layer can be done in a vacuum process such as evaporation or sputtering, or by electro-chemical means such as

electroplating (with or without electrodes). These deposited intermediate metal layers may or may not be epitaxial after deposition (depending on substrate temperature during deposition), but epitaxial orientation can subsequently be obtained during a post-deposition heat treatment.

In certain embodiments, solution coating processes can be used for deposition of one or a combination of any of the oxide layers on textured substrates; however, they can be particularly applicable for deposition of the initial (seed) layer on a textured metal substrate. The role of the seed layer is to provide 1) protection of the substrate from oxidation during deposition of the next oxide layer when carried out in an oxidizing atmosphere relative to the substrate (for example, magnetron sputter deposition of yttria-stabilized zirconia from an oxide target); and 2) an epitaxial template for growth of subsequent oxide layers. In order to meet these requirements, the seed layer should grow epitaxially over the entire surface of the metal substrate and be free of any contaminants that may interfere with the deposition of subsequent epitaxial oxide layers.

The formation of oxide buffer layers can be carried out so as to promote wetting of an underlying substrate layer. Additionally, in particular embodiments, the formation of metal oxide layers can be carried out using metal alkoxide precursors (for example, "sol gel" precursors), in which the level of carbon contamination can be greatly reduced over other known processes using metal alkoxide precursors.

This heating step can be carried out after, or concurrently with, the drying of excess solvent from the sol gel precursor film. It must be carried out prior to decomposition of the precursor film, however.

The carbon contamination accompanying conventional oxide film preparation in a reducing environment (e.g., 4%H_2-Ar) is believed to be the result of an incomplete removal of the organic components of the precursor film. The presence of carbon-containing contaminants C_xH_y and $C_aH_bO_c$ in or near the oxide layer can be detrimental, since they can alter the epitaxial deposition of subsequent oxide layers. Additionally, it is likely that the trapped carbon-containing contaminants buried in the film can be oxidized during the processing steps for subsequent oxide layers, which can utilize oxidizing atmospheres. The oxidation of the carbon-containing

contaminants can result in CO_2 formation, and the subsequent blistering of the film, and possible delamination of the film, or other defects in the composite structure. Thus, it is undesirable to allow carbon-containing contaminants arising from metal alkoxide decomposition to become oxidized only after the oxide layer is formed. Preferably, the carbon-containing contaminants are oxidized (and hence removed from the film structure as CO_2) as the decomposition occurs. Also the presence of carbon-containing species on or near film surfaces can inhibit the epitaxial growth of subsequent oxide layers.

According to particular embodiments, after coating a metal substrate or buffer layer, the precursor solution can be air dried, and then heated in an initial decomposition step. Alternatively, the precursor solution can be directly heated in an initial decomposition step, under an atmosphere that is reducing relative to the metal substrate. Once the oxide layer initially nucleates on the metal substrate in the desired epitaxial orientation, the oxygen level of the process gas is increased, for example, by adding water vapor or oxygen. The nucleation step requires from about 5 minutes to about 30 minutes to take place under typical conditions.

These methods are described in U.S. Patent Application Serial No. _________, filed on even date herewith, and entitled "Enhanced Purity Oxide Layer Formation."

In certain embodiments, an epitaxial buffer layer can be formed using a low vacuum vapor deposition process (e.g., a process performed at a pressure of at least about $1x10^{-3}$ Torr). The process can include forming the epitaxial layer using a relatively high velocity and/or focused gas beam of buffer layer material.

The buffer layer material in the gas beam can have a velocity of greater than about one meter per second (e.g., greater than about 10 meters per second or greater than about 100 meters per second). At least about 50% of the buffer layer material in the beam can be incident on the target surface (e.g., at least about 75% of the buffer layer material in the beam can be incident on the target surface, or at least about 90% of the buffer layer material in the beam can be incident on the target surface).

The method can include placing a target surface (e.g., a substrate surface or a buffer layer surface) in a low vacuum environment, and heating the target

surface to a temperature which is greater than the threshold temperature for forming an epitaxial layer of the desired material on the target surface in a high vacuum environment (e.g., less than about $1x10^{-3}$ Torr, such as less than about $1x10^{-4}$ Torr) under otherwise identical conditions. A gas beam containing the buffer layer material and optionally an inert carrier gas is directed at the target surface at a velocity of at least about one meter per second. A conditioning gas is provided in the low vacuum environment. The conditioning gas can be contained in the gas beam, or the conditioning gas can be introduced into the low vacuum environment in a different manner (e.g., leaked into the environment). The conditioning gas can react with species (e.g., contaminants) present at the target surface to remove the species, which can promote the nucleation of the epitaxial buffer layer.

The epitaxial buffer layer can be grown on a target surface using a low vacuum (e.g., at least about $1x10^{-3}$ Torr, at least about 0.1 Torr, or at least about 1 Torr) at a surface temperature below the temperature used to grow the epitaxial layer using physical vapor deposition at a high vacuum (e.g., at most about $1x10^{-4}$ Torr). The temperature of the target surface can be, for example, from about 25°C to about 800°C (e.g., from about 500°C to about 800°C, or from about 500°C to about 650°C).

The epitaxial layer can be grown at a relatively fast rate, such as, for example, at least about 50 Angstroms per second.

These methods are described in U.S. Patent No. 6,027,564, issued February 22, 2000, and entitled "Low Vacuum Process for Producing Epitaxial Layers;" U.S. Patent No. 6,022, 832, issued February 8, 2000, and entitled "Low Vacuum Process for Producing Superconductor Articles with Epitaxial Layers;" and/or commonly owned U.S. Patent Application No. 09/007,372, filed January 15, 1998, and entitled "Low Vacuum Process for Producing Epitaxial Layers of Semiconductor Material."

In some embodiments, a buffer layer can be formed using ion beam assisted deposition (IBAD). In this technique, a buffer layer material is evaporated using, for example, electron beam evaporation, sputtering deposition, or pulsed laser deposition while an ion beam (e.g., an argon ion beam) is directed at a smooth surface of a substrate onto which the evaporated buffer layer material is deposited.

For example, the buffer layer can be formed by ion beam assisted deposition by evaporating a buffer layer material having a rock-salt like structure (e.g., a material having a rock salt structure, such as an oxide, including MgO, or a nitride) onto a smooth, amorphous surface (e.g., a surface having a root mean square roughness of less than about 100 Angstroms) of a substrate so that the buffer layer material has a surface with substantial alignment (e.g., about 13° or less), both in-plane and out-of-plane.

The conditions used during deposition of the buffer layer material can include, for example, a substrate temperature of from about 0°C to about 400°C (e.g., from about room temperature to about 400°C), a deposition rate of from about 1.0 Angstrom per second to about 4.4 Angstroms per second, an ion energy of from about 200 eV to about 1200 eV, and/or an ion flux of from about 110 microamperes per square centimeter to about 120 microamperes per square centimeter.

In some embodiments, the substrate is formed of a material having a polycrystalline, non-amorphous base structure (e.g., a metal alloy, such as a nickel alloy) with a smooth amorphous surface formed of a different material (e.g., Si_3N_4).

In certain embodiments, a plurality of buffer layers can be deposited by epitaxial growth on an original IBAD surface. Each buffer layer can have substantial alignment (e.g., about 13° or less), both in-plane and out-of-plane.

These methods are described in PCT Publication No. WO 99/25908, published on May 27, 1999, and entitled "Thin Films Having A Rock-Salt-Like Structure Deposited on Amorphous Surfaces."

In some embodiments, an epitaxial buffer layer can be deposited by sputtering from a metal or metal oxide target at a high throughput. Heating of the substrate can be accomplished by resistive heating or bias and electric potential to obtain an epitaxial morphology. A deposition dwell may be used to form an oxide epitaxial film from a metal or metal oxide target.

The oxide layer typically present on substrates can be removed by exposure of the substrate surface to energetic ions within a reducing environment, also known as Ion Beam etching. Ion Beam etching can be used to clean the substrate prior to film deposition, by removing residual oxide or impurities from the substrate, and

producing an essentially oxide-free preferably biaxially textured substrate surface. This improves the contact between the substrate and subsequently deposited material. Energetic ions can be produced by various ion guns, for example, which accelerate ions such as Ar^+ toward a substrate surface. Preferably, gridded ion sources with beam voltages greater than 150 ev are utilized. Alternatively, a plasma can be established in a region near the substrate surface. Within this region, ions chemically interact with a substrate surface to remove material from that surface, including metal oxides, to produce substantially oxide-free metal surface.

Another method to remove oxide layers from a substrate is to electrically bias the substrate. If the substrate tape or wire is made negative with respect to the anode potential, it will be subjected to a steady bombardment by ions from the gas prior to the deposition (if the target is shuttered) or during the entire film deposition. This ion bombardment can clean the wire or tape surface of absorbed gases that might otherwise be incorporated in the film and also heat the substrate to elevated deposition temperatures. Such ion bombardment can be further advantageous by improving the density or smoothness of the epitaxial film.

Upon formation of an appropriately textured, substantially oxide-free substrate surface, deposition of a buffer layer can begin. One or more buffer layers, each including a single metal or oxide layer, can be used. In some preferred embodiments, the substrate is allowed to pass through an apparatus adapted to carry out steps of the deposition method of these embodiments. For example, if the substrate is in the form of a wire or tape, the substrate can be passed linearly from a payout reel to a take-up reel, and steps can be performed on the substrate as it passes between the reels.

According to some embodiments, substrate materials are heated to elevated temperatures which are less than about 90% of the melting point of the substrate material but greater than the threshold temperature for forming an epitaxial layer of the desired material on the substrate material in a vacuum environment at the predetermined deposition rate. In order to form the appropriate buffer layer crystal structure and buffer layer smoothness, high substrate temperatures are generally preferred. Typical lower limit temperatures for the growth of oxide layers on metal

are approximately 200°C to 800°C, preferably 500°C to 800°C, and more preferably, 650°C to 800°C. Various well-known methods such as radiative heating, convection heating, and conduction heating are suitable for short (2 cm to 10 cm) lengths of substrate, but for longer (1m to 100 m) lengths, these techniques may not be well suited. Also to obtain desired high throughput rates in a manufacturing process, the substrate wire or tape must be moving or transferring between deposition stations during the process. According to particular embodiments, the substrates are heated by resistive heating, that is, by passing a current through the metal substrate, which is easily scaleable to long length manufacturing processes. This approach works well while instantaneously allowing for rapid travel between these zones. Temperature control can be accomplished by using optical pyrometers and closed loop feedback systems to control the power supplied to the substrate being heated. Current can be supplied to the substrate by electrodes which contact the substrate in at least two different segments of the substrate. For example, if the substrate, in the form of a tape or wire, is passed between reels, the reels themselves could act as electrodes. Alternatively, if guides are employed to transfer the substrate between reels, the guides could act as electrodes. The electrodes could also be completely independent of any guides or reels as well. In some preferred embodiments, current is applied to the tape between current wheels.

In order that the deposition is carried out on tape that is at the appropriate temperature, the metal or oxide material that is deposited onto the tape is desirably deposited in a region between the current wheels. Because the current wheels can be efficient heat sinks and can thus cool the tape in regions proximate to the wheels, material is desirably not deposited in regions proximate to the wheels. In the case of sputtering, the charged material deposited onto the tape is desirably not influenced by other charged surfaces or materials proximate to the sputter flux path. For this reason, the sputter chamber is preferably configured to place components and surfaces which could influence or deflect the sputter flux, including chamber walls, and other deposition elements, in locations distant from the deposition zone so that they do not alter the desired linear flux path and deposition of metal or metal oxide in regions of the tape at the proper deposition temperature.

More details are provided in commonly owned United States Patent Application Serial No. 09/500,701, filed on February 9, 2000, and entitled "Oxide Layer Method," and commonly owned United States Patent Application Serial No. ________, filed on even date herewith, and entitled "Oxide Layer Method."

In preferred embodiments, three buffer layers are used. A layer of Y_2O_3 or CeO_2 (e.g., from about 20 nanometers to about 50 nanometers thick) is deposited (e.g., using electron beam evaporation) onto the substrate surface. A layer of YSZ (e.g., from about 0.2 micron to about 1 micron thick, such as about 0.5 micron thick) is deposited onto the surface of the Y_2O_3 or CeO_2 layer using sputtering (e.g, using magnetron sputtering). A CeO_2 layer (e.g., about 20 nanometers thick) is deposited (e.g, using magnetron sputttering) onto the YSZ surface. The surface of one or more of these layers can be chemically and/or thermally conditioned as described herein.

In certain embodiments, the underlying layer (e.g., a buffer layer or a different superconductor layer) can be conditioned (e.g., thermally conditioned and/or chemically conditioned) so that the superconductor layer is formed on a conditioned surface. The conditioned surface of the underlying layer can be biaxially textured (e.g., (113)[211]) or cube textured (e.g., (100)[011] or (100)[011]), have peaks in an X-ray diffraction pole figure that have a full width at half maximum of less than about 20° (e.g., less than about 15°, less than about 10°, or from about 5° to about 10°), be smoother than before conditioning as determined by high resolution scanning electron microscopy or atomic force microscopy, have a relatively high density, have a relatively low density of impurities, exhibit enhanced adhesion to other material layers (e.g., a superconductor layer or a buffer layer) and/or exhibit a relatively small rocking curve width as measured by x-ray diffraction.

"Chemical conditioning" as used herein refers to a process which uses one or more chemical species (e.g., gas phase chemical species and/or solution phase chemical species) to affect changes in the surface of a material layer, such as a buffer layer or a superconductor material layer, so that the resulting surface exhibits one or more of the above noted properties.

"Thermal conditioning" as used herein refers to a process which uses elevated temperature with or without chemical conditioning to affect changes in the surface of

a material layer, such as a buffer layer or a superconductor material layer, so that the resulting surface exhibits one or more of the above noted properties. Preferably, thermal conditioning occurs in a controlled environment (e.g., controlled gas pressure, controlled gas environment and/or controlled temperature).

Thermal conditioning can include heating the surface of the underlying layer to a temperature at least about 5°C above the deposition temperature or the crystallization temperature of the underlying layer (e.g., from about 15°C to about 500°C above the deposition temperature or the crystallization temperature of the underlying layer, from about 75°C to about 300°C above the deposition temperature or the crystallization temperature of the underlying layer, or from about 150°C to about 300°C above the deposition temperature or the crystallization temperature of the underlying layer). Examples of such temperatures are from about 500°C to about 1200°C (e.g., from about 800°C to about 1050°C). Thermal conditioning can be performed under a variety of pressure conditions, such as above atmospheric pressure, below atmospheric pressure, or at atmospheric pressure. Thermal conditioning can also be performed using a variety of gas environments (e.g., an oxidizing gas environment, a reducing gas environment, or an inert gas environment).

"Deposition temperature" as used herein refers to the temperature at which the layer being conditioned was deposited.

"Crystallization temperature" as used herein refers to the temperature at which a layer of material (e.g., the underlying layer) takes on a crystalline form.

Chemical conditioning can include vacuum techniques (e.g., reactive ion etching, plasma etching and/or etching with fluorine compounds, such as BF_3 and/or CF_4). Chemical conditioning techniques are disclosed, for example, in Silicon Processing for the VLSI Era, Vol. 1, eds. S. Wolf and R.N. Tanber, pp. 539-574, Lattice Press, Sunset Park, CA, 1986.

Alternatively or additionally, chemical conditioning can involve solution phase techniques, such as disclosed in Metallurgy and Metallurgical Engineering Series, 3d ed., George L. Kehl, McGraw-Hill, 1949. Such techniques can include contacting the surface of the underlying layer with a relatively mild acid solution (e.g., an acid solution containing less about 10 percent acid, less than about two

percent acid, or less than about one percent acid). Examples of mild acid solutions include perchloric acid, nitric acid, hydrofluoric acid, hydrochloric acid, acetic acid and buffered acid solutions. In one embodiment, the mild acid solution is about one percent aqueous nitric acid. In certain embodiments, bromide-containing and/or bromine-containing compositions (e.g., a liquid bromine solution) can be used to condition the surface of a buffer layer or a superconductor layer.

This method can be used to form multiple buffer layers (e.g., two, three, four, or more buffer layers), with one or more of the buffer layers having a conditioned surface.

The method can also be used to form multiple superconductor layers, with one or more of the superconductor layers having a conditioned surface. For example, a superconductor layer can be formed and then thermally and/or chemically conditioned as described above. An additional superconductor layer can then be formed on the conditioned surface of the first superconductor layer. This process can be repeated as many times as desired.

These methods are described in commonly owned U.S. Provisional Patent Application No. 60/166, 140, filed November 18, 1999, and entitled "Multi-Layer Articles and Methods of Making Same," and commonly owned U.S. Patent Application Serial No. ______, filed on even date herewith, and entitled "Multi-layer Articles and Methods of Making Same".

Superconducting articles formed from such precursor compositions can include more than one superconductor layer (e.g., two superconductor layers disposed on each other). The combined thickness of the superconductor layers can be at least about one micron (e.g., at least about two microns, at least about three microns, at least about four microns, at least about five microns, or at least about six microns). The combined critical current density of the superconductor layers can be at least about $5x10^5$ Amperes per square centimeter (e.g., at least about $1x10^6$ Amperes per square centimeter, or at least about $2x10^6$ Amperes per square centimeter).

The metal oxyfluoride is converted into an oxide superconductor at a rate of conversion selected by adjusting temperature, vapor pressure of gaseous water or both. For example, the metal oxyfluoride can be converted in a processing gas having

a moisture content of less than 100% relative humidity (e.g., less than about 95% relative humidity, less than about 50% relative humidity, or less than about 3% relative humidity) at 25°C to form some oxide superconductor, then completing the conversion using a processing gas having a higher moisture content (e.g., from about 95% relative humidity to about 100% relative humidity at 25°C). The temperature for converting the metal oxyfluoride can be in the range of from about 700°C to about 900°C (e.g., from about 700°C to about 835°C). The processing gas preferably contains from about 1 volume percent oxygen gas to about 10 volume percent oxygen gas.

These methods are described in PCT Publication No. WO 98/58415, published on December 23, 1998, and entitled "Controlled Conversion of Metal Oxyfluorides into Superconducting Oxides".

In particular embodiments, methods can be employed to minimize the formation of undesirable a-axis oriented oxide layer grains, by inhibiting the formation of the oxide layer until the required reaction conditions are attained.

Conventional processes developed for decomposition and reaction of fluoride-containing precursors use a constant, and low, non-turbulent flow of process gas that is introduced into the decomposition furnace in an orientation that is parallel to the film surface, resulting in a stable boundary layer at the film/gas interface. In the apparatus types typically used for oxide layer precursor decomposition and reaction, the diffusion of gaseous reactants and products through this gas/film boundary layer appears to control the overall reaction rates. In thin, small area films (for example, less than about 0.4 microns thick and less than about a square centimeter), the diffusion of H_2O into the film and the diffusion of HF out of the film occur at rates such that the formation of the $YBa_2Cu_3O_{7-x}$ phase does not begin at any significant rate until the sample reaches the processing temperature. However, as the film thickness or area increases, the rates of gaseous diffusion into and out of the film decrease, all other parameters being equal. This results in longer reaction times and/or incomplete formation of the $YBa_2Cu_3O_{7-x}$ phase, resulting in reduced crystallographic texture, lower density, and reduced critical current density. Thus, the

overall rate of $YBa_2Cu_3O_{7-x}$ phase formation is determined, to a significant extent, by the diffusion of gases through the boundary layer at the film surface.

One approach to eliminating these boundary layers is to produce a turbulent flow at the film surface. Under such conditions, the local gas composition at the interface is maintained essentially the same as in the bulk gas (that is, the pH_2O is constant, and the pHF is approximately zero). Thus, the concentration of the gaseous products/reactants in the film is not controlled by the diffusion through the gas/film surface boundary layer condition, but rather by diffusion through the film. In order to minimize the nucleation of a-axis $YBa_2Cu_3O_{7-x}$ oriented grains on a substrate surface, the formation of the $YBa_2Cu_3O_{7-x}$ phase is inhibited until desired process conditions are reached. For example, the formation of the $YBa_2Cu_3O_{7-x}$ phase can be inhibited until desired process temperature is reached.

In one embodiment, a combination of: 1) low (non-turbulent) process gas flow, so that a stable boundary layer is established at the film/gas interface, during the ramp to temperature, and 2) high (turbulent) process gas flow, so that the boundary layer is disrupted at the film/gas interface, is employed. For example, in a three inch tube furnace, the flow can be from about 0.5 to about 2.0 L/min during the temperature ramp from ambient temperature to the desired process temperature. Thereafter, the flow can be increased to a value of from about 4 to about 15 L/min during the time at which the film is being processed. Thus, the rate of formation of $YBa_2Cu_3O_{7-x}$ and epitaxial texture formation can be increased at high temperature, while minimizing the amount of unwanted a-axis nucleation and growth at low temperature during ramp up. According to these processes, a-axis nucleated grains are desirably present in an amount of less than about 1%, as determined by scanning electron microscopy.

More details are provided in commonly owned U.S. Patent Application Serial No. ______, filed on even date herewith, and entitled "Control of Oxide Layer Reaction Rates."

As desribed herein, a superconducting layer is deposited on the substrate, intermediate-coated substrate, or buffer-coated substrate, in the form of a precursor composition. Two general approaches are presented for the formulation of precursor

compositions. In both approaches, the advantages of the method will be redirected if at least a portion of the components is present in solid form. In one approach, the cationic constituents of the precursor composition are provided in components taking on a solid form, either as elements, or preferably, compounded with other elements. The precursor composition is provided in the form of ultrafine particles which are dispersed so that they can be coated onto and adhere onto the surface of a suitable substrate, intermediate-coated substrate, or buffer-coated substrate. These ultrafine particles can be created by aerosol spray, by evaporation or by similar techniques which can be controlled to provide the chemical compositions and sizes desired. The ultrafine particles are less than about 500 nm, preferably less than about 250 nm, more preferably less than about 100 nm and even more preferably less than about 50 nm. In general, the particles are less than about 50% the thickness of the desired final film thickness, preferably less than about 30% most preferably less than about 10% of the thickness of the desired final film thickness. Precursors for the preparation of ultrafine particles can be metalorganic solutions such as those disclosed in U.S. Patent No. 5,231,074 to Cima et al., PCT Publication No. WO 98/58415, published on December 23, 1998, entitled Controlled Conversion of Metal Oxyfluorides into Superconducting Oxides."

Alternatively, the precursor components can be prepared from elemental sources, or from a substantially stoichiometric compound comprising the desired constituents. For example, evaporation of a solid comprising a substantially stoichiometric compound of desired REBCO constituents (for example, $YBa_2Cu_3O_{7-x}$) or a number of solids, each containing a particular constituent of the desired final superconducting layer (for example, Y_2O_3, BaF_2, CuO) could be used to produce the ultrafine particles for production of the precursor compositions. Alternatively, spray drying or aerosolization of a metalorganic solution comprising a substantially stoichiometric mixture of desired REBCO constituents could be used to produce the ultrafine particles used in the precursor compositions.

For example, in one embodiment according to this first approach, the precursor composition comprises ultrafine particles of one or more of the constituents of the superconducting layer in a substantially stoichiometric mixture, present in a

carrier. This carrier comprises a solvent, a plasticizer, a binder, a dispersant, or a similar system known in the art, to form a dispersion of such particles.

For example, in an alternate embodiment according to this first approach, the precursor composition comprises ultrafine particles of one or more of the constituents of the superconducting layer in a substantially stoichiometric mixture, present in a carrier, the carrier being substantially as described above. Each ultrafine particle contains a substantially compositionally uniform, homogeneous mixture of such constituents. For example, each particle can contain BaF_2, and rare-earth oxide, and copper oxide or rare earth/barium/copper oxyfluoride in a substantially stoichiometric mixture. For example, analysis of such particles would reveal a rare-earth:barium:copper ratio as substantially 1:2:3 in stoichiometry, with a fluorine:barium ratio of substantially 2:1 in stoichiometry. These particles can be either crystalline, or amorphous in form.

Alternatively, in a second approach, one or more of the cationic constituents is provided in the precursor composition as a metalorganic salt or metalorganic compound, and is present in solution. The metalorganic solution acts as a solvent, or carrier, for the other solid-state elements or compounds. According to this latter approach, dispersants and/or binders can be substantially eliminated from the precursor composition. For example, in an embodiment according to this second approach, the precursor composition comprises ultrafine particles of rare-earth oxide and copper oxide in substantially a 1:3 stoichiometric ratio, along with a solublized barium-containing salt, for example, barium-trifluoroacetate dissolved in an organic solvent, such as methanol.

The substrate is desirably uniformly coated to yield a superconducting film of from about 1 to about 10 microns, preferably from about 1 to about 5 microns, more preferably from about 2 to about 4 microns.

In some embodiments, the final superconducting layer is desirably a film of the oxide complex containing rare earth:barium:copper (REBCO), in a stoichiometric ratio of 1:2:3 and an oxygen stoichiometry slightly deficient in oxygen. These complexes have the chemical formula "rare-earth"$Ba_2Cu_3O_{7-\delta}$, where "rare earth" includes yttrium, praesodium, neodymium, samarium, europium, gadolinium,

terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, lanthanum and cerium. Such complexes include $YBa_2Cu_3O_{7-x}$, also known as YBCO. The extent of oxygen deficiency (that is, the amount that the stoichiometry of oxygen in such complexes is less than 7) is somewhat variable, but can range from about 6.5 to about 6.9.

If the superconducting layer is of the REBCO type, the precursor composition can contain a rare earth element, barium, and copper in the form of their oxides; halides such as fluorides, chlorides, bromides and iodides; carboxylates and alcoholates, for example, acetates, including trihaloacetates such as trifluroracetates, formates, oxalates, lactates, oxyfluorides, propylates, citrates, and acetylacetonates, and, chlorates and nitrates. The precursor composition can include any combination of such elements (rare earth element, barium, and copper) in their various forms, which can convert to an intermediate containing a barium halide, plus rare earth oxyfluoride and copper(oxyfluoride) without a separate decomposition step or with a decomposition step that is substantially shorter than that which may be required for precursors in which all constituents are solubilized, and without substantial formation of $BaCO_3$, and which can subsequently be treated using high temperature reaction processes to yield an epitaxial REBCO film with T_c of no less than about 89K, and J_c greater than about 500,000 A/cm^2 at a film thickness of 1 micron or greater. For example, for a $YBa_2Cu_3O_{7-x}$ superconducting layer, the precursor composition could contain barium halide (for example, barium fluoride), yttrium oxide (for example, Y_2O_3), and copper oxide; or yttrium oxide, barium trifluoroacetate in a trifluoroacetate/methanol solution, and a mixture of copper oxide and copper trifluoroacetate in trifluoroacetate/methanol. Alternatively, the precursor composition could contain Ba-trifluoroacetate, Y_2O_3, and CuO. Alternatively, the precursor composition could contain barium trifluoroacetate and yttrium trifluoroacetate in methanol, and CuO. Alternatively, the precursor composition could contain BaF_2 and yttrium acetate and CuO. In some preferred embodiments, barium-containing particles are present as BaF_2 particles, or barium acetate. It is believed to be undesirable to allow the formation of barium carbonate during processing of the superconductive layer. In some embodiments the precursor could be substantially a

solublized metalorganic salt containing some or all of the cation constituents, provided at least a portion of one of the compounds containing cation constituents present in solid form.

In certain embodiments, the precursor in a dispersion includes a binder. The binder functions to hold the fine particles together as an aid in deposition on the underlying layer. Suitable binders include cellulose derivatives such as nitrocellulose, methylcellulose, hydroxyethylcellulose, carboxymethylcellulose and other cellulose derivatives known in the art. Also useful are polymeric binders and copolymeric binders such as polyvinyl binders and copolyvinyl binders including polyvinyl aldehydes and copolyvinyl aldehydes such as polyvinyl butyral polymers and copolymers. Other binders include various starches from various sources, and chemically modified starches.

Dispersants can also be included in certain embodiments. A wide variety of dispersants can be utilized in particular embodiments. For example, any organic solvents which do not solublize all precursor constituents can be used. For example, sorbitan esters, sorbitan diesters and sorbitan triesters, including sorbitan trioleate are suitable. Further suitable dispersants can readily be chosen by those of skill in the art. Dispersions can be maintained mechanically by stirring, shaking, mixing or by ultrasonic agitation.

Solvents can also be included in certain embodiments, particularly those in which a precursor composition includes a constituent salt or compound dissolved in a solvent, in addition to constituents present as ultrafine particles in a dispersion. Solvents can be any which serve to solublize a precursor constituent. For example, common volatile organic solvents including ethers such as ethyl ether, dioxane and tetrahydrofuran; esters including alkyl acetates, alkyl propionates and alkyl formates, alcohols including straight chain and branched alkanols, and other solvents such as dimethylformamide, dimethylsulfoxide and acetonitrile can be used. Other suitable solvents can readily be put to use by those of skill in the art.

The precursor compositions can be applied to substrate or buffer-treated substrates by a number of methods, which are designed to produce coatings of substantially homogeneous thickness. For example, the precursor compositions can

be applied using spin coating, slot coating, gravure coating, dip coating, tape casting, or spraying.

In some embodiments, multi-layer high temperature superconductors are provided, including first and second high temperature superconductor coated elements. Each element includes a substrate, at least one buffer layer deposited on the substrate, a high temperature superconductor layer, and optionally a cap layer. The first and second high temperature superconductor coated elements can be joined at the first and second cap layers, or can be joined with an intervening, preferably metallic, layer. Exemplary joining techniques include soldering and diffusion bonding.

Such a multi-layer architecture provides improved current sharing, lower hysteretic losses under alternating current conditions, enhanced electrical and thermal stability, and improved mechanical properties. Useful conductors can be made having multiple tapes stacked relative to one another and/or laminated to provide sufficient ampacity, dimensional stability, and mechanical strength. Such embodiments also provide a means for splicing coated tape segments and for termination of coated tape stackups or conductor elements.

Moreover, it is expected that this architecture can provide significant benefits for alternating current applications. AC losses are shown to be inversely proportional to the effective critical current density within the conductor, more specifically, the cross-sectional area within which the current is carried. For a multifilimentary conductor, this would be the area of the "bundle" of superconducting filaments, excluding any sheath material around that bundle. For a "face-to-face" architecture, the "bundle" critical current density would encompass only the high temperature superconductor films and the thickness of the cap layer structure. The cap layer can be formed of one or more layers, and preferably includes at least one noble metal layer. "Noble metal," as used herein, is a metal, the reaction products of which are thermodynamically unstable under the reaction conditions employed to prepare the HTS tape. Exemplary noble metals include, for example, silver, gold, palladium, and platinum. Noble metals provide a low interfacial resistance between the HTS layer and the cap layer. In addition, the cap layer can include a second layer of normal metal (for example, copper or aluminum or alloys of normal metals). In direct current

applications, additional face-to-face wires would be bundled or stacked to provide for the required ampacity and geometry for a given application.

Additionally, the high temperature superconductor film on the surface of the tapes could be treated to produce local breaks, that is, non-superconducting regions or stripes in the film only along the length of the tape (in the current flow direction). The cap layer deposited on the high temperature superconductor film would then serve to bridge the nonsuperconducting zones with a ductile normal metal region. An offset in the edge justification of the narrow strips or filaments, similar to a running bond brick pattern, would allow current to transfer to several narrow superconducting filaments both across the cap layers and to adjacent filaments, further increasing the redundancy and improving stability.

In all embodiments, a normal metal layer could be included along the edge of the conductor to hermetically seal the high temperature superconductor films and to provide for current transfer into the film, and if necessary, from the film into the substrate.

More details are provided in commonly owned U.S. Provisional Patent Application Serial No. 60/145,468, filed on July 23, 1999, and entitled "Enhanced High Temperature Coated Superconductors," and commonly owned United States Patent Application Serial No. _______, filed concurrently herewith, and entitled "Enhanced High Temperature Coated Superconductors".
In some embodiments, coated conductors can be fabricated in a way that minimizes losses incurred in alternating current applications. The conductors are fabricated with multiple conducting paths, each of which comprises path segments which extend across at least two conducting layers, and further extend between these layers.

Each superconducting layer has a plurality of conductive path segments extending across the width of the layer, from one edge to another, and the path segments also have a component of direction along the length of the superconducting layer. The path segments in the superconducting layer surface are in electrically conductive communication with interlayer connections, which serve to allow current to flow from one superconducting layer to another. Paths, which are made up of path segments, are periodically designed, so that current flow generally alternates between

two superconducting layers in bilayered embodiments, and traverses the layers through interlayer connections.

Superconducting layers can be constructed to contain a plurality of path segments which extend both across their widths and along their lengths. For example, superconducting layers can be patterned so as to achieve a high resistivity or a fully insulating barrier between each of the plurality of path segments. For example, a regular periodic array of diagonal path segments can be imposed on the layer along the full length of the tape. Patterning of superconducting layers to give such arrays can be accomplished by a variety of means known to those skilled in the art, including for example, laser scribing, mechanical cutting, implantation, localized chemical treatment through a mask, and other known methods. Further, the superconducting layers are adapted to allow the conductive path segments in their surfaces to electrically communicate with conducting interlayer connections passing between the layers, at or near their edges. The interlayer connections will typically be normally conducting (not superconducting) but in special configurations could also be superconducting. Interlayer connections provide electrical communication between superconducting layers which are separated by non-conducting or highly resistive material which is positioned between the superconducting layers. Such non-conducting or highly resistive material can be deposited on one superconducting layer. Passages can be fabricated at the edges of the insulating material to allow the introduction of interlayer connections, followed by deposition of a further superconducting layer. One can achieve a transposed configuration with coated conductors by patterning a superconducting layer into filaments parallel to the axis of the tape and winding the tape in a helical fashion around a cylindrical form.

More details are provided in commonly owned United States Patent Application Serial No. 09/500,718, filed on February 9, 2000, and entitled "Coated Conductors with Reduced AC Loss." The invention will be further described in the following examples, which do not limit the scope of the invention described in the claims.

EXAMPLES

Starting Materials Properties

Barium acetate was purchased from Alfa Aesar (Ward Hill, MA) as crystalline particles, 99.0 to 102.0% (assay), stock number 12198. Trifluoracetic acid was purchased from Alfa Aesar, stock number 31771. Semiconductor grade methanol was purchased from Alfa Aesar, stock number 19393. 1% and 10% solutions of nitrocellulose in amyl acetate were purchased from Ernest Fullham, Inc.

Yttrium oxide was purchased from Nanophase Technologies Corp. (Burr Ridge, IL), as 99.5% purity (total rare earth oxide) particles, product code 1600. The manufacturer's stated average particle size was 17-30 nm, as determined by BET analysis of specific surface area. Barium fluoride was purchased from Alfa Aesar as 99% pure (assay) particles, with less than 40 mesh particle size, stock number 12338. To reduce particle size, the as-received barium fluoride was jet-milled to a best-effort particle size reduction by Jet Pulverizer Co. (Palmyra, New Jersey). Copper oxide particles were purchased from Nanophase Technologies, Inc. as 99.5+% pure particles, product code 0500. The manufacturer's stated average particle size was 16-32 nm, as determined by BET analysis of the specific surface area.

The Y_2O_3 and CuO particles were investigated by transmission electron microscopy. The as-received particles were typically spherical, individually less than about 50 nm in diameter, and bridged into networks. Barium fluoride was investigated by scanning electron microscopy before and after jet-milling. Before milling, the particles appeared blocky and smaller than the 40 mesh size specified by the manufacturer. The jet-milled particles appeared more uniform in size and were less blocky.

Purity of materials was investigated by inductively coupled plasma/atomic emission spectroscopy (ICP/AES). The nanophase Y_2O_3 was assayed as 91% pure, BaF_2 as 88% pure and CuO as 99.4% pure. These materials were also examined for the presence of common impurities, which are shown in Table 1. These materials were not baked prior to analysis, and the major contaminant in Y_2O_3 and BaF_2 was

presumed to be moisture. Jet-milling did not appear to introduce additional contaminants.

Table 1. Impurities present in Raw Materials (wt. %)

Material	Al	Ca	Cl	Fe	K	Na	S	Si	Sr	Ti	Zn	heavy metals
Y_2O_3	0.013	0.043		0.008		NPD	0.020	0.001	NPD	NPD	NPD	
CuO	NPD	NPD		NPD		NPD	NPD	NPD	NPD	0.003	0.080	
BaF_2 (as received)	0.229			0.012		0.442		3.63	1.06			
BaF_2 (milled)	0.231			NPD		0.438		3.94	1.05			
$Ba(CO_2CH_3)_2$		0.007	0.0006	0.0004	0.03	0.002			0.07			0.0004

The Θ-2Θ X-ray diffraction (XRD) pattern of the as-received Y_2O_3 matched the monoclinic phase of this material. The XRD patterns for BaF_2 before and after milling matched the pattern for frankdicksonite, which is a cubic pattern. The XRD pattern of the as-received CuO matched the pattern for the monoclinic (tenorite) phase of this material.

The results of the particle size measurements of Y_2O_3, BaF_2 and CuO particles are presented in Table 2.

Table 2. Particle Size Measurements (microns)

Material	Particle size as measured by inventors (time-of-flight)		Particle size as measured by manufacturer (agitation)	
	mean	Std. Dev.	Mean	Std.dev.
Y_2O_3	0.64	1.83	0.21	0.17
CuO	0.46	1.88	0.13	0.041
BaF_2 (as received)	1.3	1.77	-	-
BaF_2 (milled)	0.78	1.42	-	-

Differences in the sizes of Y_2O_3 and CuO particles as measured by Nanophase Technologies, Inc. and our measurements are likely due to differences in the methods used and the effectiveness of each method at breaking up loose agglomerates. A dry aerosol time-of-flight method was used, and Nanophase Technologies, Inc. dispersed the particles in a liquid that was ultrasonically agitated during the measurement. The inventors' analysis is likely indicative of agglomerate and individual particles. Jet-milling of BaF_2 successfully resulted in reduction of particle size, as well as tightening the size distribution.

Example 2: Demonstration of Epitaxial Film Growth

Three precursor slurries were prepared, as summarized in Table 3. Two of the precursors were prepared by dispersing Y_2O_3 and CuO into Ba-trifluoroacetate (Ba-TFA) dissolved in methanol, with differences in the amount of methanol used. The Ba-TFA was made by dissolving barium acetate in water, then adding trifluoroacetic

acid. The trifluoroacetic acid replaced the acetate group on the barium. The aqueous Ba-TFA solution was then vacuum dried, and the Ba-TFA obtained from the drying operation was dissolved in methanol. A third dispersion was made by dispersing Y_2O_3, BaF_2, and CuO in a 3% solution of nitrocellulose in amyl acetate. The yttrium molarity was calculated as (moles Y)/(volume of solution + volume of solids in dispersion). The stoichiometry of these precursors, determined by ICP/AES, is presented in Table 4.

Table 3. Precursor Description

dispersion	Y source	Ba source	Cu source	Dispersing liquid	Y molarity
A	Y_2O_3	Ba-TFA	CuO	MeOH	~0.37
B	Y_2O_3	Ba-TFA	CuO	MeOH	0.64
C	Y_2O_3	BaF_2	CuO	3% nitrocellulose/amyl acetate	0.50

Table 4. Stoichiometry of Precursor Materials determined by ICP/AES

Dispersion	Molar ratio (normalized to Y=1)		
	Y	Ba	Cu
A	1	1.99	2.95
B	1	1.91	2.96
C	1	1.80	3.02

Comparison of superconducting films was made between a metalorganic deposition (MOD) process, and the inventive deposition process. The MOD process employed yttrium acetate, barium acetate, and copper acetate. Each salt was dissolved in water, fluorinated with trifluoroacetic acid, and vacuum dried. The dried salts were then dissolved in methanol to produce the yttrium/barium/copper (YBC) solution for coating. Control of the precursor chemistry, and hence the stoichiometry, is very precise.

Critical current density (J_c) development experiments were performed on CeO_2-capped yttria-stabilized zirconia (CeO/YSZ) single crystals, except sample AP9

(described below), which was coated onto single crystal strontium titanate. YSZ single crystals were purchased from CrysTec GMBH (Berlin, Germany) as 10 x 10 x 0.5 mm wafers with a (100) normal orientation, one side polished to R_a = 0.179 nm. 20 nm of cerium oxide was sputter-deposited on the surface of these wafers, then post-annealed in an oxygen atmosphere for one hour at 950°C. The CeO/YSZ system was chosen because these are the materials typically employed as the top two buffer layers in development of coated conductor articles. Table 5 provides a summary of the samples that were fully processed and measured electrically. Samples which were processed for development of coating and decomposition cycles but not reacted or measured are not included.

Table 5. Precursor Reaction Conditions and Properties of Superconducting Layers

Sample ID	Precursor	Coat method	Decomposition time (hours)	Reaction time (hours)	Final thickness (microns)	J_c (MA/cm^2) minimum	T_c (K)	ΔT (K)
AP6	A	Spin	4.3	5	1.2	0.15	87.3	1.5
AP9	A	Spin	0.5	8	1.2	0.13		
AP18	A	Spin	0.5	5	0.66	0.40		
AP19	A	Spin	0.5	5	0.65	0.28		
AP20	A	Spin	0.5	4	0.81	0.30		
AP21	B	Spin	0.5	6	2.6	0.35		
AP22	B	Spin	0.25 + 0.25	8	2.1	0.42	89.6	1.1
AP23	B	Spin	0.25	4	1.5	0.50	89.3	1.4
AP29	C	Spin	0.5	8	1.1	0	89.7	1.5
AP30	C	Dip	0.5	8	3.5	0	90.1	1.8
Baseline	MOD	Spin	3	1	0.4	4.5	92-93	1-2
Baseline	MOD	Spin	3+3	2	0.8	2.5	92-93	1-2
Baseline	MOD	Spin	3+3+3	3	1.2	2	92-93	1-2
Baseline	MOD	Spin	3+3+3+3	3	1.5	0.6	92-93	1-2

The time from first introduction to the furnace to the start of cool down was recorded as the decomposition time. The furnace profile used to decompose sample AP6 is shown in Fig. 4, the profile used for samples AP9-AP20, and for samples AP29-AP30 is shown in Fig. 5, and the profile used for samples AP22-AP23 is shown in Fig. 6. For comparison, the typical profile used for decomposing an MOD film is shown in Fig. 7. Multiple decomposition times indicated in Table 5 specify that

samples were repeatedly coated and decomposed as often as necessary to achieve film thickness before reaction. Upon completion of the decomposition cycle, the samples were patterned to form bridges to enable I_c measurement, with the exception of sample AP18, which was patterned after reaction.

The XRD pattern of AP6, which was typical of all scans run on decomposed solid-state precursor-coated CeO/YSZ is shown in Fig. 8. For comparison, a typical scan of MOD-coated lanthanum aluminate is shown in Fig. 9. The BaF_2 peak at 24.8° in the pattern generated from the MOD-coated sample was shifted to a slightly higher angle, whereas this same peak was not shifted in the scan of the samples according to the invention.

The isothermal hold time at peak temperature was recorded as the reaction time. The furnace profile used for reaction of all samples, except for sample AP9, which had a 735°C peak temperature isothermal hold, is shown in Fig. 10.

The XRD pattern of the 1.5 micrometer thick sample AP23 after reaction to form $YBa_2Cu_3O_{7-\delta}$ is shown in Fig. 11. The pattern clearly indicates c-axis texture for the fully converted YBCO film. For comparison, the XRD pattern of a baseline 1.2μm thick MOD-coated CeO/YSZ substrate is shown in Fig. 12. Figs. 13 and 14, respectively, show expanded scales of the scans in Figs. 11 and 12, indicating that in both systems, a $BaCeO_3$ reaction product was formed. The phase content and c-axis texture of YBCO films formed by the two methods on CeO/YSZ were similar.

Pole figure analysis was performed using a dedicated Siemens X-ray system with a 2-D detector system to increase analysis speed and sensitivity. Fig. 15 shows the (102) YBCO pole figure for sample AP21, which had a relatively weak biaxial texture. Fig. 16 shows the (102) YBCO pole figure for the 0.5 micrometer thick sample AP18, which had a stronger biaxial texture. As a comparison, the pole figure analysis of a baseline 0.8 μm thick MOD-coated and reacted film is shown in Fig. 17.

The thickness of the films used in the measured bridge after reaction were measured by scanning the bridge depth using a white light interferometer. Some conservatism is built into the J_c calculations due to such measurements. Since the

film surface is relatively low density and rough, the average thickness taken from the rough surface is greater than the actual current-carrying dimension.

The surfaces of coated and reacted films were examined optically at 8x, 62x, and 500x magnification. Some surfaces were also examined by scanning electron microscopy (SEM) to gain an understanding of the general morphology of the films.

The general surface morphology of the inventive films is similar to that of the baseline MOD films, although the MOD films appear denser and perhaps smaller in "grain" size. The sizes of the surface features are likely functions of both processing parameters (time, temperature) and thickness. It is not clear whether this surface density difference is due to the relative thickness of the samples or if it represents an inherent difference in the YBCO structures produced by the different methods.

Example 3: Characterization of Superconducting Film Properties

Bridges were patterned on the samples after decomposition by physically scribing parallel lines to define the bridge. Silver pads were deposited onto the fully converted film surface using thermal evaporation to provide for current input and voltage taps. Samples were immersed in liquid nitrogen and critical current density (I_c) measured using the standard four-point measurement technique and a 1 μvolt/cm criterion. This method is known to those of skill in the art. To calculate J_c, the I_c was divided by the average measured thickness and the width of each bridge as determined from optical analysis. Transport transition temperatures (T_c) were measured by cooling the samples in helium vapor across their transition temperature. J_c and I_c results are shown above in Table 5.

Samples made from precursors A and B delivered J_c in the range from 0.13 to 0.50 MA/cm^2 in thicknesses ranging from 0.65 to 2.6 μm. The samples made from precursor C exhibited superconducting transition, but the J_c were virtually zero. The high level of impurities in the BaF_2 component of this precursor might have been a likely cause contributing to the poor current carrying performance of these samples.

$T_{c'}$ values for these inventive samples ranged from 87.3 to 90.1, with ΔT_c values ranging from 1.1-1.8 K. For comparison, typical $T_{c'}$ values in baseline MOD films are 90-92 K, with ΔT_c values of 1-2°. These results show that the inventive method can produce thick superconducting films of performance equal to the baseline MOD process, especially for film thickness above about 1.5 microns.

Example 4: Long Length Coating Process

To evaluate long length coating behavior, precursor B was web coated onto a fine silver strip. The silver strip was purchased from Cimini and Associates, Inc. (Pawcatuck, CT) and was 3 meters long, 1 inch wide x 0.003 inches thick, and was in the half hard condition.

Precursor B was applied to the silver as a 18.2 μm thick layer, which corresponds to a 1.5 μm final reacted YBCO layer thickness. A syringe pump delivered the precursor at 0.77 ml/min into a 14 mm wide stainless steel slot die applicator, which had a 0.004 inch slot height. The precursor was agitated in an ultrasonic bath before fluid was drawn into the syringe, and approximately four minutes elapsed before the beginning region of the 3 m length was coated. The gap between the applicator and the web was 0.005 inches, and line speed was 3 meter/min. Approximately 3 m of silver was coated and allowed to air-dry before being wrapped into a coil.

Four 10 cm length pieces were cut at intervals along the length and digested entirely in 10% HNO_3 for ICP/AES analysis to determine compositional drift over the length of the 3 meter coating. The Y-Ba-Cu molar ratios from these samples are plotted in Fig. 18. The data indicate that the Ba/Y ratio stayed roughly constant over the length of the tape. Such measurement can also be carried out by other techniques, for example, by Auger spectroscopy, by diffuse infrared Fourier transform spectroscopy, or by energy dispersive analysis by X-ray.

Samples cut from 12, 98, 173 and 267 cm along the length of the tape were decomposed per the cycle shown in Fig. 5. XRD patterns of these decomposed samples are shown in Fig. 19. No differences were apparent in their phase content.

These samples were then reacted for 7 hours according to the thermal profile of Fig. 10. The XRD patterns of the reacted samples are shown in Fig. 20.

The results presented herein indicate that the J_c obtained for the inventive method of preparing superconducting layers are already on the order of 25-50% of the highest J_c obtained for YBCO films of comparable thickness below about 1 micron derived from optimized metalorganic solution processes. The performance of films produced by the inventive processes is comparable to that of the films produced by the baseline MOD process under the same growth conditions, for films with thicknesses greater than about 1.5 micrometers. The inventive process also eliminates the complex decomposition thermal cycle without producing any of the known defects (i.e. cracks, blisters, dewetting) of the MOD processes. These results indicate no fundamental limitation to performance of the solid-state derived precursor films, and significant improvement in economics and process robustness. The precursors could be converted to biaxially textured YBCO films with no strong evidence of second phase formation, even for precursors that were not strictly stoichiometric.

It will be apparent to one of skill in the art that the reaction conditions specifically disclosed herein can be further optimized according to routine experimentation. It is, for example, well known that YBCO reaction processes, and resulting film structure and properties, are strongly affected by such variables as temperature, water and oxygen content in the reaction gas, and gas dynamics within the furnace.

OTHER EMBODIMENTS

It is to be understood that while the invention has been described in conjunction with the detailed description thereof, the foregoing description is intended to illustrate and not limit the scope of the invention, which is defined by the scope of the appended claims. Other aspects, advantages, and modifications are within the scope of the following claims.

What is claimed is:

1. A precursor composition for the production of superconductive films, said precursor comprising particles of at least one precursor constituent; and a dispersant containing said particles, producing a dispersion of said particles.

2. The precursor composition of claim 1, wherein said particles have diameters of less than about 500 nm.

3. The precursor composition of claim 2, wherein said particles have diameters of less than about 250 nm.

4. The precursor composition of claim 3, wherein said particles have diameters of less than about 50 nm.

5. The precursor composition of claim 1, wherein said particles comprise a rare earth element, barium, and copper.

6. The precursor composition of claim 5, wherein said rare earth element, barium, and copper are present in an elemental ratio of substantially 1:2:3, respectively.

7. The precursor composition of claim 6, wherein said precursor comprises: particles comprising a rare earth element; particles comprising barium; and particles comprising copper.

8. The precursor composition of claim 7, wherein said rare earth element is in a compound in the form of a rare earth oxide, a rare earth halide, or a rare earth nitride.

9. The precursor composition of claim 7, wherein said barium is in a compound in the form of a barium halide, or barium halocarboxylate.

10. The precursor composition of claim 7, wherein said copper is in a compound in the form of a copper oxide, copper halide, or elemental copper.

11. The precursor composition of claim 1, wherein said precursor comprises particles, each of said particles comprising a rare earth element, barium and copper.

12. The precursor composition of claim 11, wherein said rare earth element, barium, and copper are present in an elemental ratio of substantially 1:2:3, respectively.

13. The precursor composition of claim 11, wherein said rare earth element is in a compound in the form of a rare earth oxide, a rare earth oxyfluoride, a rare earth halide, or a rare earth nitride.

14. The precursor composition of claim 11, wherein said barium is in a compound in the form of a barium halide, a barium oxyfluoride, or barium halocarboxylate.

15. The precursor composition of claim 14, wherein said barium halocarboxylate is barium trifluoroacetate, or barium fluoride.

16. The precursor composition of claim 11, wherein said copper is in a compound in the form of a copper oxide, a copper oxyfluoride, a copper halide, or is in the form of elemental copper.

17. The precursor composition of claim 5, wherein said rare earth element is yttrium.

18. The precursor composition of claim 5, wherein said particles comprise yttrium oxide and copper oxide.

19. The precursor composition of claim 18, wherein said particles further comprise barium halide or barium halocarboxylate.

20. The precursor composition of claim 19, wherein said barium halocarboxylate is barium trifluoroacetate.

21. The precursor composition of claim 18, wherein said barium is in the form of a compound which is convertible to a barium halide.

22. The precursor composition of claim 1, wherein at least one precursor constituent is solublized.

23. The precursor composition of claim 22, wherein said solubilized constituent is barium trifluoroacetate.

24. The precursor composition of claim 22, wherein said solubilized constituent is yttrium trifluoroacetate.

25. The precursor composition of claim 22, wherein said solubilized constituent is copper trifluoroacetate.

26. The precursor composition of claim 22, wherein said solubilized constituents are barium trifluoroacetate, and yttrium trifluoroacetate.

27. The precursor composition of claim 22, wherein said solubilized constituent is barium trifluoroacetate , yttrium trifluoroacetate, and copper trifluoroacetate, wherein a portion of said copper constituent is not solubilized.

28. A method of making a multilayer article, said method comprising providing a layer of a first material adapted to form a surface, said first material comprising a buffer material and a substrate material; and disposing a layer of second material on the layer of said first material, wherein said second material comprises a dispersion of particles.

29. The method of claim 28, wherein said first material comprises at least one buffer material.

30. The method of claim 29, wherein said surface is biaxially textured.

31. The method of claim 28, wherein said particles comprise precursor materials, wherein said precursor materials comprise a rare earth element, barium, and copper.

32. The method of claim 31, wherein said barium is present as a barium halide or barium halocarboxylate.

33. The method of claim 28, wherein said particles have diameters of less than about 500 nm.

34. The method of claim 33, wherein said particles have diameters of less than about 250 nm.

35. The method of claim 34, wherein said particles have diameters of less than about 250 nm.

36. The method of claim 31, wherein said barium is convertible to barium halide or barium halocarboxylate.

37. A coated conductor tape prepared with the precursor composition of claim 1, comprising an HTS film with critical current density of greater than 500,000 A/cm^2 at a thickness of 1 micrometer.

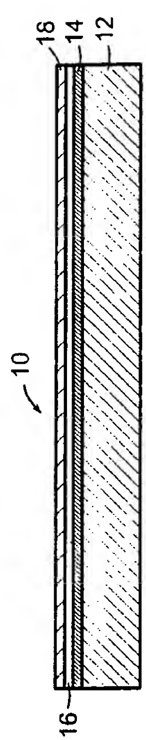


FIG. 1

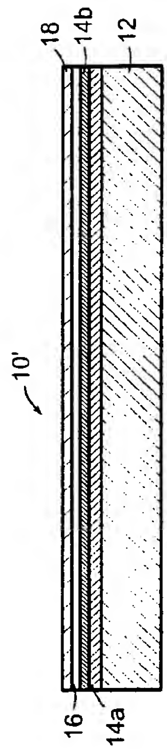


FIG. 2

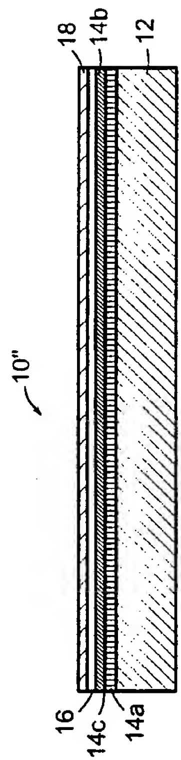


FIG. 3

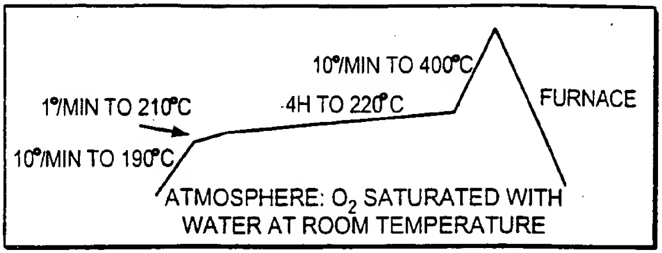


FIG. 4

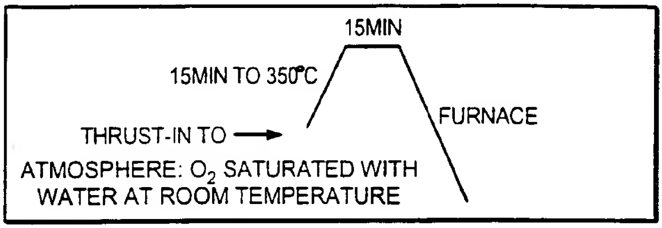


FIG. 5

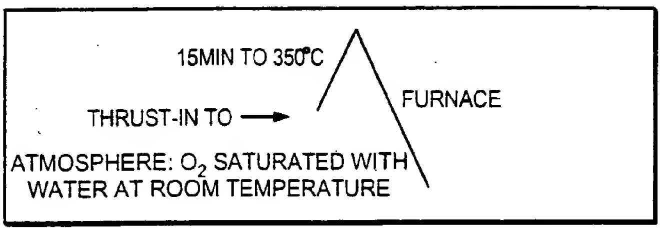


FIG. 6

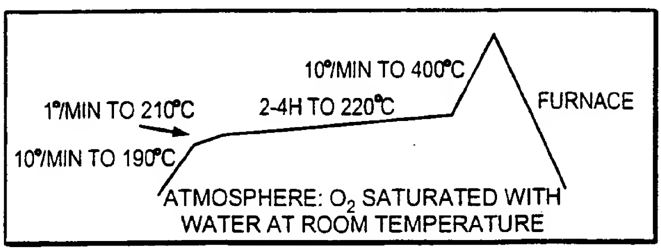
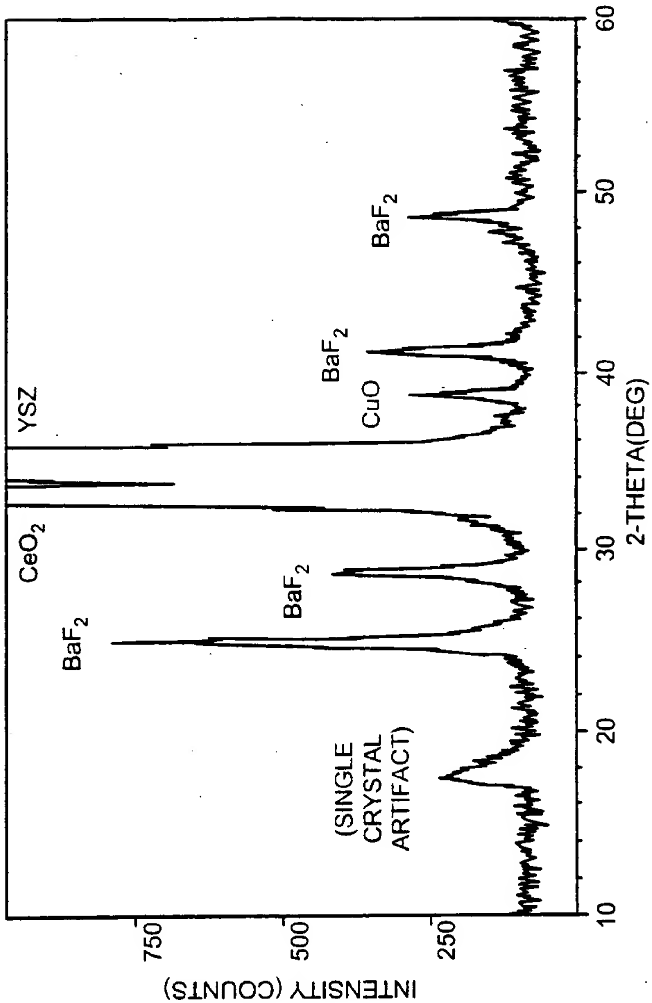


FIG. 7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20
30
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50
60
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BaF2
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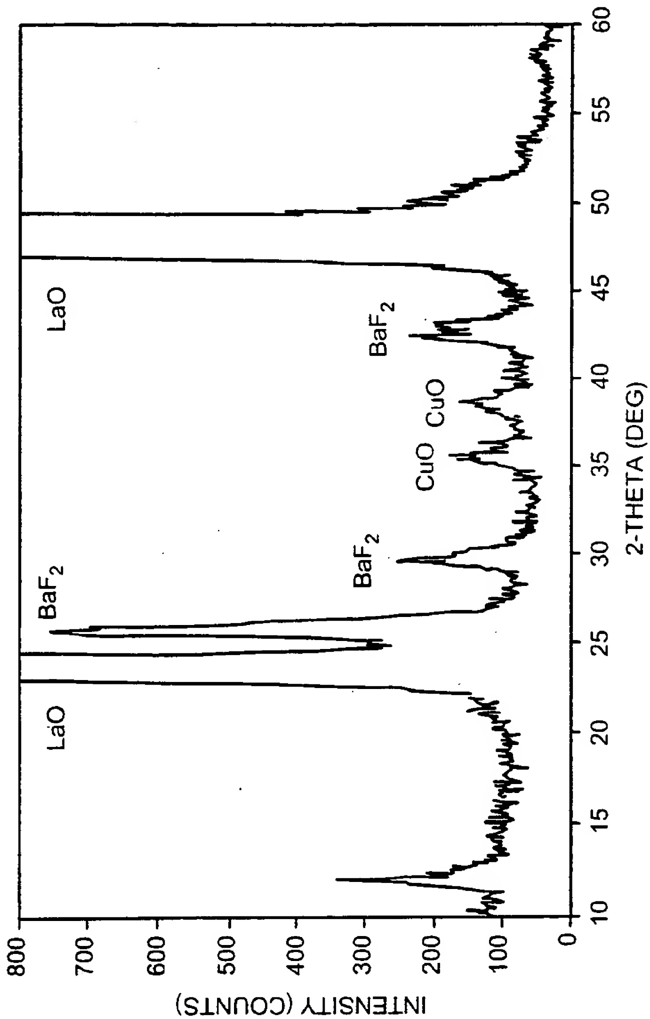
YSZ
CuO
BaF2
BaF2

FIG. 8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BaF2
BaF2
CuO
CuO
BaF2
LaO
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600
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35
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45
50
55
60
2-THETA (DEG)

FIG. 9

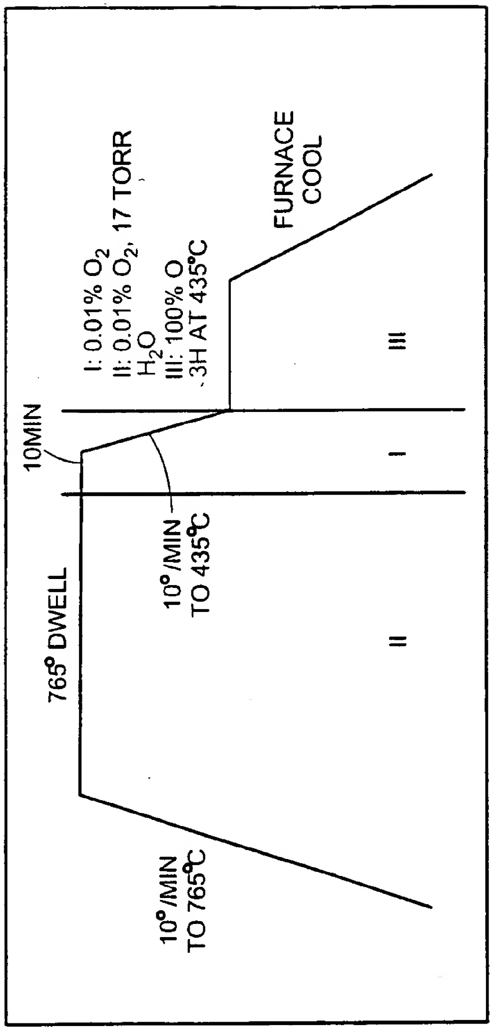
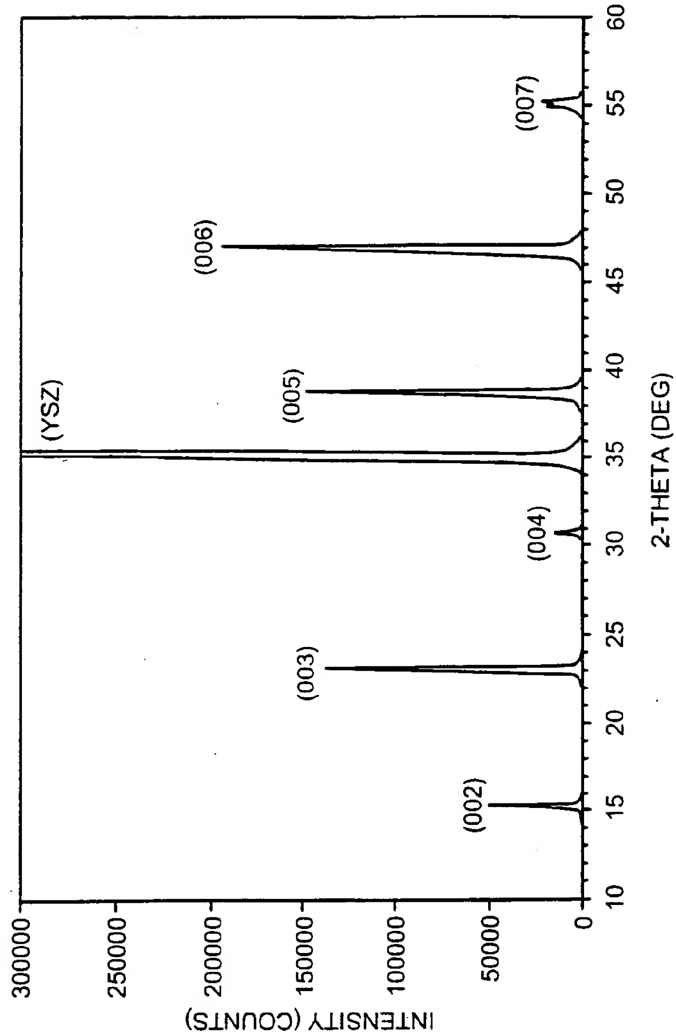

10°/MIN
TO 765°C
765° DWELL
10°/MIN
TO 435°C
10MIN
I: 0.01% O_2
II: 0.01% O_2, 17 TORR
H_2O
III: 100% O
3H AT 435°C
FURNACE
COOL
II
I
III

FIG. 10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200000
150000
100000
50000
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2-THETA (DEG)
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20
25
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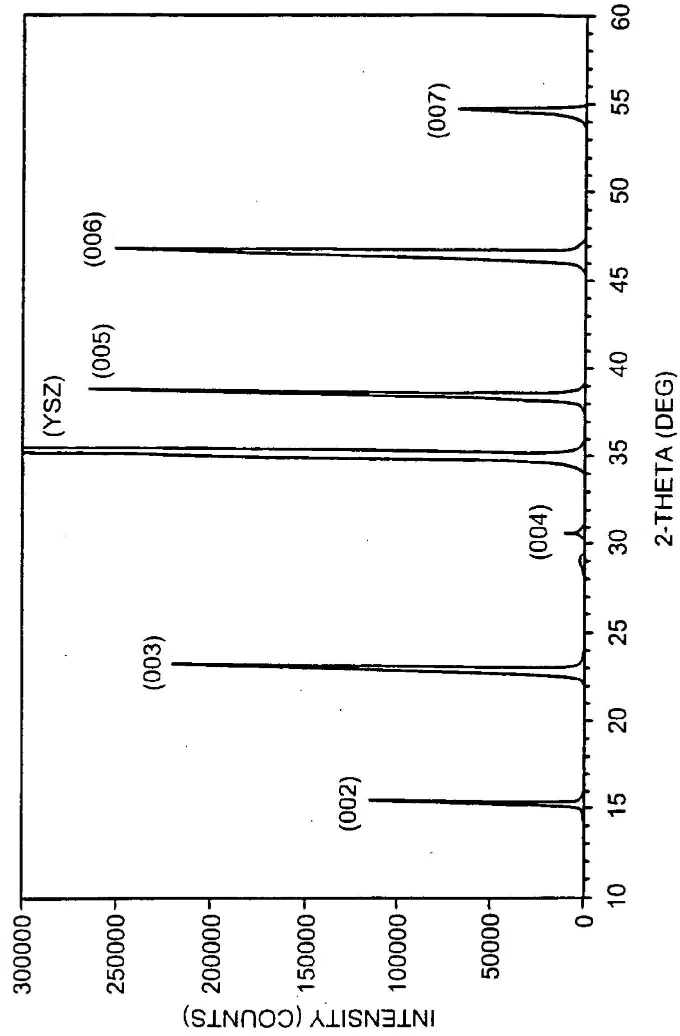
35
40
45
50
55
60
(002)
(003)
(004)
(YSZ)
(005)
(006)
(007)

FIG. 11


(002)
(003)
(004)
(YSZ)
(005)
(006)
(007)
10
15
20
25
30
35
40
45
50
55
60
2-THETA (DEG)
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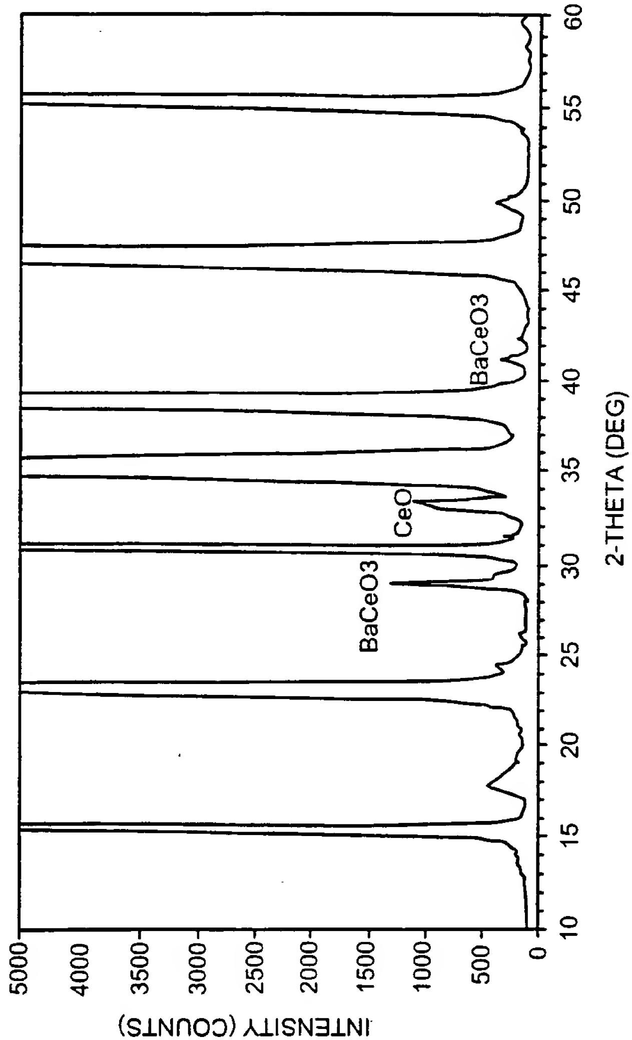
100000
150000
200000
250000
300000
INTENSITY (COUNTS)

FIG. 12


BaCeO3
CeO
BaCeO3
2-THETA (DEG)
INTENSITY (COUNTS)
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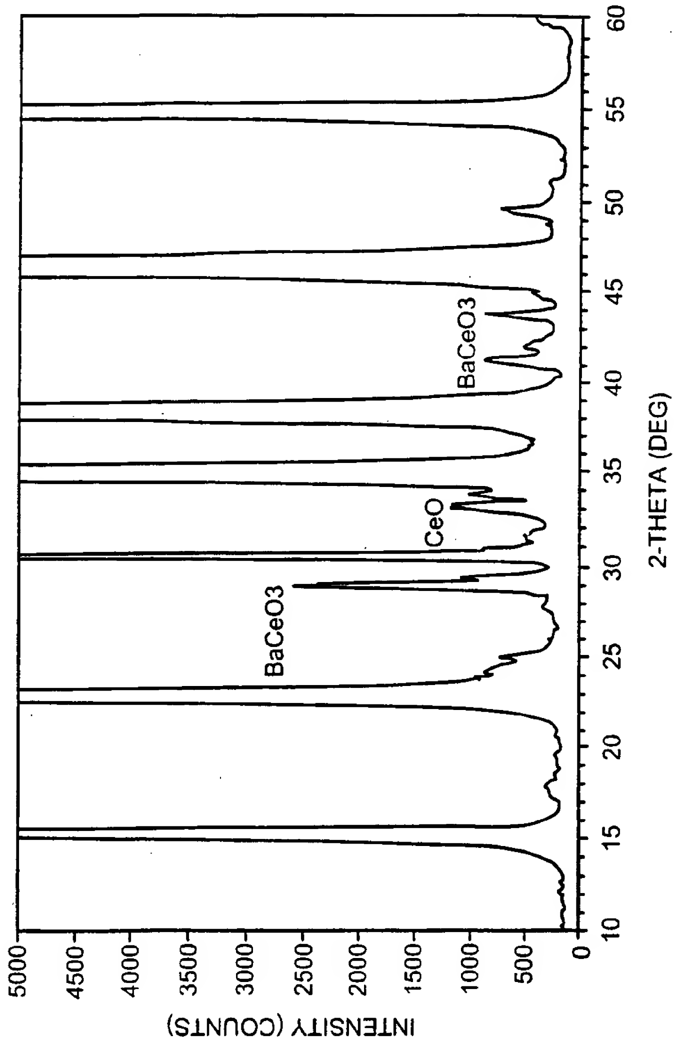
0 500 1000 1500 2000 2500 3000 3500 4000 5000

FIG. 13


BaCeO3
CeO
BaCeO3
INTENSITY (COUNTS)
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4000
3500
3000
2500
2000
1500
1000
500
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60
2-THETA (DEG)

FIG. 14

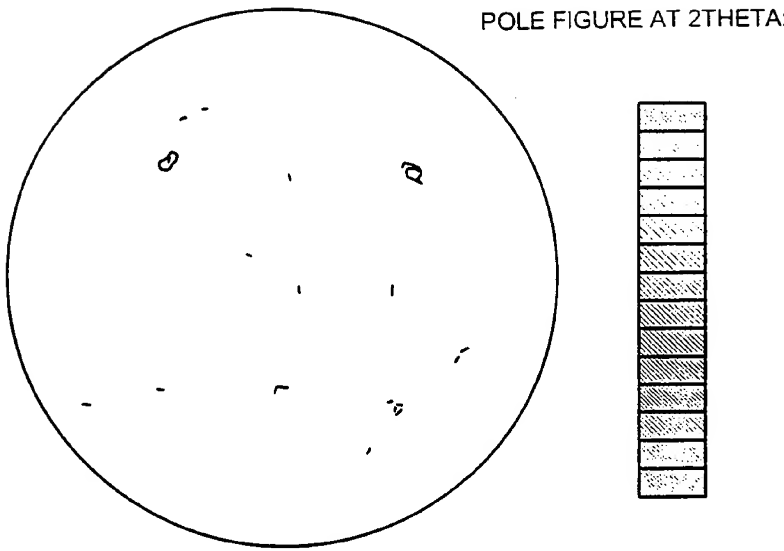


FIG. 15

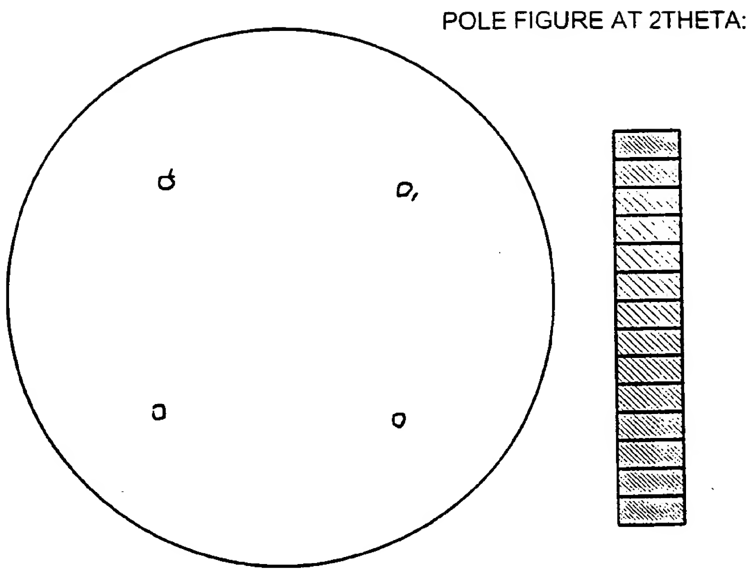


FIG. 16

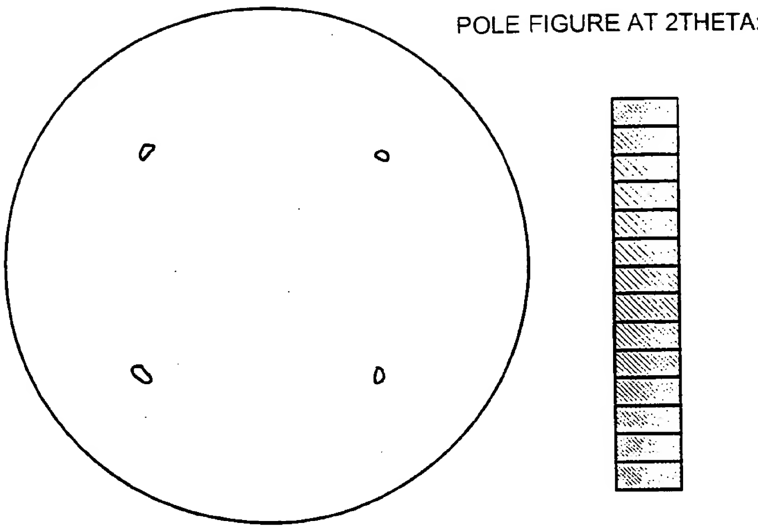


FIG. 17

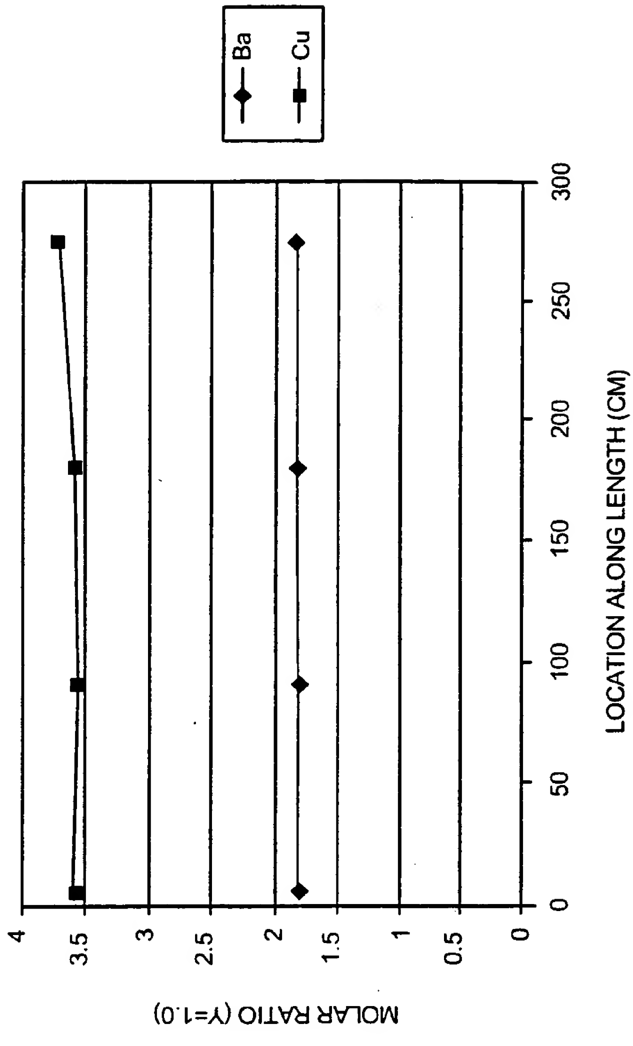
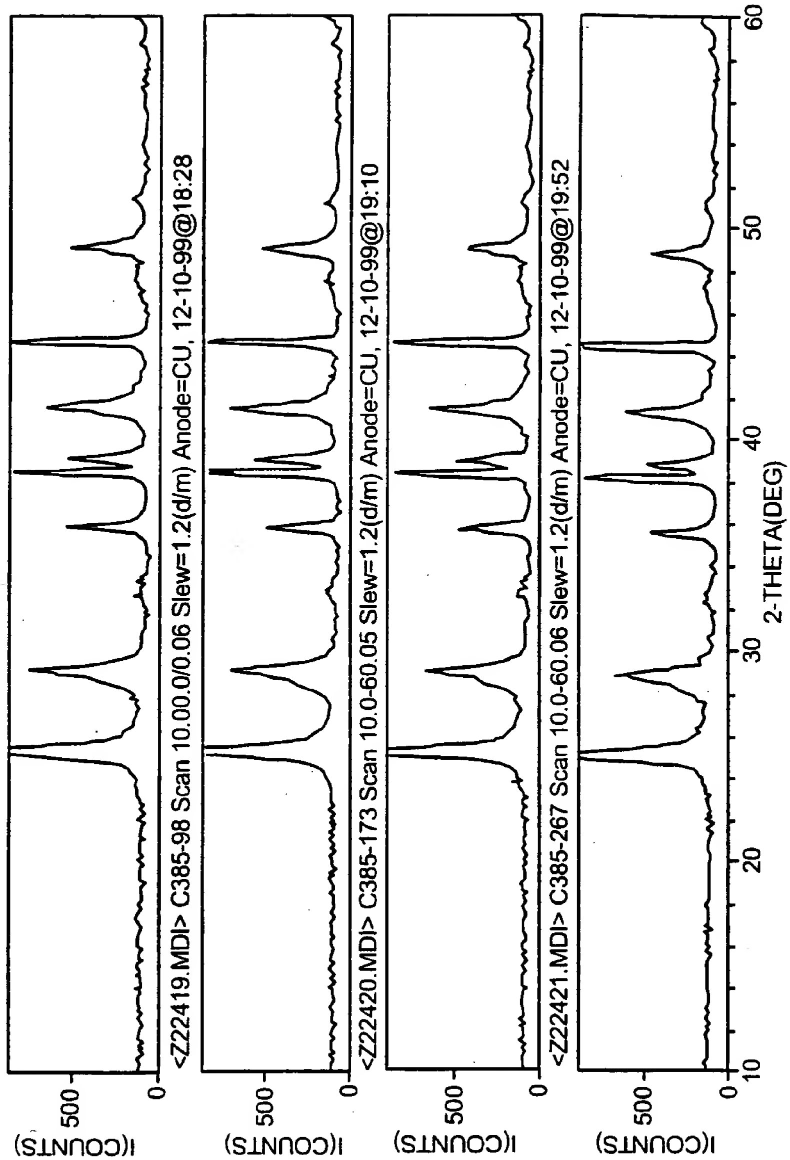

Ba
Cu
MOLAR RATIO (Y=1.0)
4
3.5
3
2.5
2
1.5
1
0.5
0
0
50
100
150
200
250
300
LOCATION ALONG LENGTH (CM)

FIG. 18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0
10
20
30
40
50
60
2-THETA(DEG)

FIG. 19

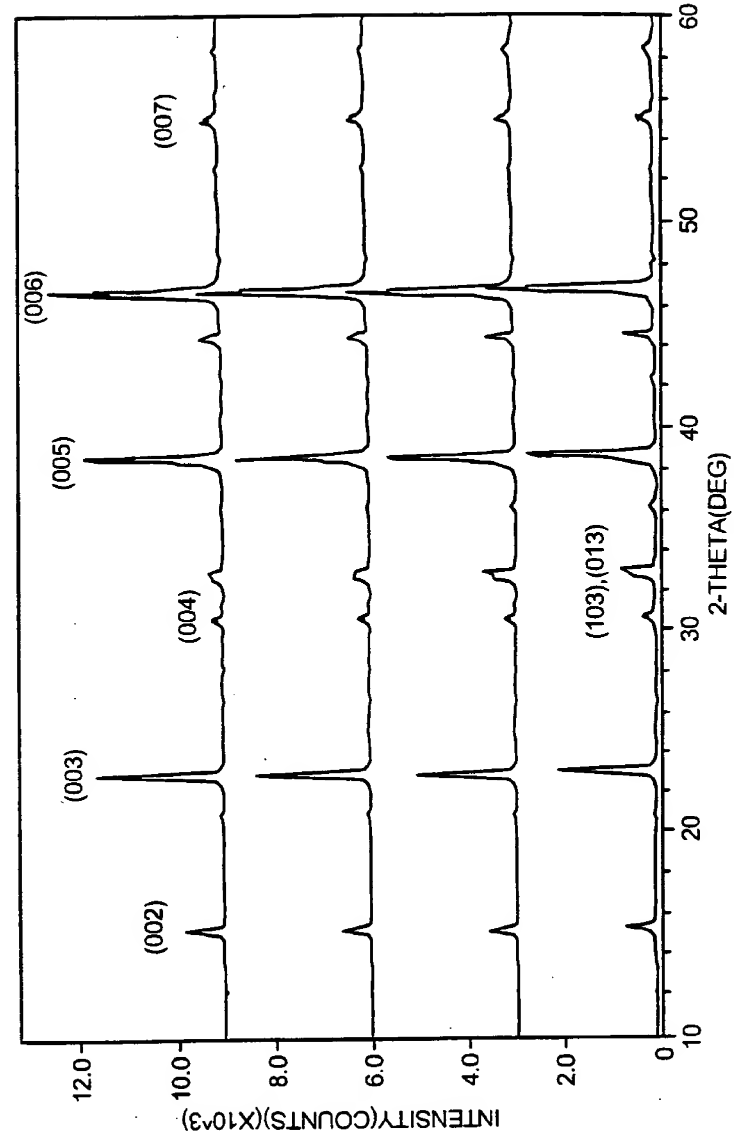
(002)
(003)
(004)
(005)
(006)
(007)
(103),(013)
INTENSITY(COUNTS)(X10^3)
12.0
10.0
8.0
6.0
4.0
2.0
0
10
20
30
40
50
60
2-THETA(DEG)

FIG. 20

INTERNATIONAL SEARCH REPORT

Inter   nal Application No
PCT/US 00/19344

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01L39/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 387 525 A (ASEA BROWN BOVERI) 19 September 1990 (1990-09-19) abstract	1
X	WO 99 35083 A (WILLEMS FRANK ;RIEDEL GUENTHER (DE); AVENTIS RES & TECH GMBH & CO) 15 July 1999 (1999-07-15) abstract	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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